Swami Ramanand Teerth Marathwada University, Nanded

-: Name of the Research Topic :-

“Studies on Li & Mn Doped NiO Thin films”

Faculty of Science in the subject Physics

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2023

“Studies on Li & Mn Doped NiO Thin films”

Abstract of proposed work plan / problem :

In the present work nanoparticle Li & Mn doped Nio thin films are to be prepared by chemical methods. This method is economical, time saving, less labour work and mechanically automated. Thin films characterization like optical, electrical, compositional, structural are to be studies by using XRD, SEM, TEM, EDAX, UV, IR, photo electrochemical characterization techniques etc.

Introduction:

The synthesis of nanoparticles (NPs) is now a focus of scientific investigation due to its unique electrical, magnetic, optical, and catalytic capabilities. As a result, when compared to conventional and commercial bulk materials, they are excellent choices for biological, optical, and electrical applications. Metal oxide nanoparticles are distinguished from bulk metals by their The creation of nanoparticles low melting temperatures, large specific surface area, superior mechanical strength, and enhanced optical and magnetic characteristics. Metal oxide thin films are crucial in chemistry, physics, and material science.

Transition metal oxides are important semiconductors with scientific and industrial uses in magnetic storage media, solar energy conversion, electronics, and catalysis. Furthermore, metal oxides with multivalent oxidation states have piqued the interest of specialists due to a wide range of intriguing and unique qualities such as nontoxicity, eco-friendliness, and long-term stability.

Transition metal oxide thin films such as NiO, ZnO, TiO_2, Fe_2O_3, and CuO have recently received increased interest for their applications in magnetic storage media, resonance imaging, bio separation, medicine, and wastewater treatment. Among many metal oxides, nickel oxide (NiO) is one of the most common p-type oxide semiconductors and attracts a lot of attention because of its excellent optical, electrical, physical, and magnetic characteristics. NiO with a low band gap

of 1.2 eV is widely employed in a variety of applications, including s3olar cells. Electrochemical devices, gas sensors, solar cells, high efficiency thermal conducting materials, magnetic recording media, and solar energy transformation are all examples of solar energy transformation.

Doping with different transition metals can change the structural, optical, and electrical characteristics of pure NiO thin films. There are various publications in the literature that employ transition metals for doping, such as nickel, cobalt, tin (Sn), lithium (Ln), cadmium (cd), zinc (Zinc), manganese(Mn), and others.

The lithium-doped nickel oxide (L-NiO) films were synthetized using the modified spray pyrolysis method with a two-step grown process. By observing the spectra of X-ray photoemission spectroscopy of L-NiO films, the intensity of Ni 2p3/2 peak of Ni3+ bonding state increases with increasing Li concentration that causes the decrease of transparency and resistivity. The L-NiO films with optimum characteristics were obtained at Li = 8 at%, where a p-type resistivity of 4.1 × 10−1 Ω cm and optical transparency above 76% in the visible region are achieved.

Literature Survey:

- **Chia-Ching (2013)** et al. In this study The lithium-doped nickel oxide (L-NiO) films were produced in two steps using a modified spray pyrolysis approach. Observing the X-ray photoemission spectra of L-NiO films, the strength of the Ni 2p3/2 peak of the Ni3+ bonding state increases with increasing Li concentration, resulting in a decrease in transparency and resistivity. The best L-NiO films were formed at Li = 8 at%, where a p-type resistivity of 4.1 101 cm and optical transparency exceeding 76% in the visible range were obtained they used : Modified spray pyrolysis method.

- **P. Mallick(2010)** et al. In this study the structural and magnetic characteristics of Ni1xMnxO (x = 0 to 0.05) produced chemically are reported. No impurity phases were found in NiO with an XRD resolution of up to 5% Mn doping. Mn doping has no effect on the fcc structure or the lattice parameter of the host NiO matrix. The average crystallite size in NiO was found to be practically constant (28 nm) up to 3 at.% Mn doping, then drops to 21 nm for 5 at.% Mn doping. The magnetic characteristics, on the other hand, changed dramatically with Mn doping. While 0 and 1 at.% Mn doped NiO exhibited antiferromagnetic behaviour down to 10 K, 3 and 5 at.% Mn doped NiO exhibited superparamagnetic behaviour at 300 K. with the bloking temp. of 186 & 171k respectively. In this study they used TEM,TPMS,etc mehod
- **Kejun Xu(2023)** et al. In this study, hydrothermal nanoflake Lidoped NiO electrochromic films were made, and the films demonstrated better electrochromic capabilities in the LiOH electrolyte. Doping with Li+ ions improved the ion transmission rates of the NiO films, thus promoting ion transport from the electrolyte into the NiO films. Finally, the simulation calculations revealed that Li doping lowered the adsorption strengths of the NiO films to OH, reducing the production and breakdown of NiOOH and aiding in the improvement of the films' cycle stabilities. As a result, the study provided in this article gives an approach for future electrochromic.

  To relax the structural configurations, we employed the Perdew-Burke-Ernzerhof (PBE) generalised gradient approximation (GGA) exchange-correlation (XC) functionals.
- **Hungru Chen(2012)** et al. In this study they used the HSE06 hybrid functional and the density functional theory (DFT) + U technique to calculate density functionals on Li0.125Ni0.875O. Both techniques reveal that, according to prior computations, the system is best represented with the hole localised on the nickel ion (which is therefore technically Ni3+) rather than in the oxygen valence band. We analyse the experimental results in light of this discovery and demonstrate that it is compatible with the existing data.

- **Víctor Hugo López-Lugo(2023)** et al. The fabrication of NiO film by To make NiO and Li-doped NiO thin films, an automated ultrasonic pyrolysis spray technique was employed with nickel acetylacetonate and lithium acetate dihydrate as metal precursors and dimethylformamide as solvent. The influence of lithium concentration in the precursor solution on structural, morphological, and electrical characteristics was investigated. XRD values vary from 21 to 25 nm, with no discernible relationship to the Li doping level. AFM research reveals that the crystallites form round-shaped aggregates and that all of the films are smooth. The optical transmittance of the films ranges from 60% to 77%, with a rising trend as the Li content increases. The electrical analysis reveals that the films are p-type, with the carrier concentration, resistivity, and carrier mobility varying depending on the amount of lithium doped. NiO: Li (10%) films, as well as Mn-doped ZnS andZnO:Al films, were effectively integrated into inorganic light emitting diodes using the same ultrasonic spray pyrolysis process. Result are prepared using XRD,SEM, atomic force microscopy (AFM) and UV- Spectrometer.
- **Lakshmi S Nair(2017)** et al. In this study it could be attributed completely to the size effect, because when the concentration of Sn was raised to 10%, the ferromagnetism disappeared and the sample became super paramagnetic. When the Sn doping concentration is increased to >5%, the lattice rapidly expands. Changes in the XRD revealed significant structural abnormalities, which were apparently caused by more interstitial incorporation of Sn. The variations in coercivity values of Sn doped samples led to the conclusion that the Sn doped samples underwent a transition from multidomain to single domain configuration, and the samples became super paramagnetic. Study is carried out by XRD and FIIR analysis.

- **Aarti S. Bhatt (2020)** et al. In this work Nanostructured NiO and Li-ion doped NiO were synthesised using a simple microwave process and modelledusing first principles. Field Emission Spectroscopy was used to investigate the impact of microwaves on the morphology of nanostructures. X-ray diffraction measurements validate the particles' nanosize and preferred orientations along the (111), (200), and (220) planes, indicating the cubic structure. The optical band gap shrinks from 3.3 eV in pure NiO to 3.17 eV in NiO doped with 1% Li. Additionally, computational simulations were usedto better understand the optical behaviour of the synthesised nanoparticles. Using photoluminescence (PL) spectroscopy, the optical characteristics of the doped materials reveal violet, blue, and green emissions. NiO nanoparticles demonstrate improved electrical capabilities and cyclability in the presenceof Li-ions. The results of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) reveal that doping NiO with 1% Li improves its reversibility and conductance value significantly. The findings are promising since the synthesised nanoparticles have a greater possibility of being employed as an active material in electrochromic, electro-optic, and supercapacitor applications.
- **Jiangyong Lio(2020)** et al. In this study they present an effective electronic structural modification of intrinsic NiO sheets by Mn-doping for styrene oxidation. Under optimised reaction conditions, a 75.0% yield of STO may be obtained by doping NiO with just a little amount of Mn (Mn/Ni atomic ratio of 0.030), which is 2.13 times greater than that of pure NiO. Furthermore, the catalyst is stable and has strong recycling performance. The improved performance is due to the synergistic impact of the plentiful Ni(II) species, the abundant oxygen vacancy sites, and the huge number of surface redox centres. This paper reports on new results of elemental-doping-induced multifunctionality in the creation of potent catalysts for the efficient and selective oxidation of styrene and other compounds. Study is carried out by XRD and SEM analysis

- **Xu Han(2019)** et al. In this study MnNiO NSAs displayed twice greater specific capacitance than pure NiO NSAs at a current density of 5 mA cm2 and superior stability with no capacitance loss after 10 000 cycles at 30 mA cm2. Furthermore, the hybrid supercapacitor device of MnNiO NSAs//grapheneCNT shown outstanding recycling stability after 50 000 charging/discharging cycles at 6 A g1 with comparable energy density and power density. . Study is carried out by XRD TEM And HRTEM analysis
- **Kiran N. Patel (2018)** et al. In this work The Ni1xMnxO (x = 0.00, 0.02, 0.04 and 0.06) nanoparticles were created using chemical precipitation and calcination at 500 C for 4 hours. Energy dispersive X-ray analysis (EDAX), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR), and vibrating sample magnetometer (VSM) were used to characterise the generated samples. The structural phase purity is confirmed by Rietveldrefinement of XRD data, and the XRD patterns are well indexed to a NaCl- like rock salt fcc crystal structure with Fm-3m space group. The particle size of Mn doped samples is less than that of pure NiO**.** However, when Mn concentration increases, particle size increases somewhat due to surface/grain boundary diffusion. Raman and FT-IR spectroscopy were used to study the vibrational characteristics of the synthesised nanoparticles.

  A core-shell model is used to explain the results of room temperature magnetization (M-H) and temperature dependent magnetization (M-T) experiments. At ambient temperature, the nanoparticles exhibit modest ferromagnetic and superparamagnetic behaviour.

Motivation :

In comparison to other transition metal oxides (such as ZnO, SnO2, TiO2, and NiO), the synthesis and characterisation of NiO thin films is the least investigated, making it an appealing target for research. Furthermore, one of the most essential approaches to change the material characteristics is to dope semiconductor nanoparticles with impurity metal ions.

Objective :

1. To prepare thin films of Nickel oxide NiO, Li doped NiO and Mn doped NiO by chemical method.
2. To study the effect of Li and Mn dopant on structural, morphological, optical properties of NiO thin films for its better applications in variousfields.

Hypothesis of Research :

The research work is directed to prepared Li and Mn doped NiO thin films. In this Work we proposed to have improved structural, optical properties of pure NiO thin films by doping of Li and Mn.

Research Methodology :

Thin Film Deposition

In recent years, extensive efforts have been made in the preparation, characterization And Application of metal oxides thin films. Thin film deposited by various techniques such as Electrochemical deposition. Pulsed laser deposition, sol gel spin coating methods, and Chemical spray pyrolysis. In the present study, we propose to use chemical method for Preparing pure and doped NiO thin film.

Characterization :

The prepared thin films will be characterized as follows :

- Structural properties by X-ray diffraction (XRD) measurement
- Surface morphology study by Scanning Electron Microscopy (SEM)
- Optical properties by UV-Vis Spectroscopy

Chapter Scheme

Chapter 1: Introduction.

Chapter 2: Experimental and characterization techniques.

Chapter 3: Result and analysis of Li doped NiO thin films.

Chapter 4: Result and analysis of Mn doped NiO thin films.

Chapter 5: Conclusion and scope for future.

Proposed Work Plan :

Year – wise plan of work and targets to achieve.

Year I – Plan:

In the first year we will do literature survey on Li and Mn doped NiO thin films. The literature includes collection of Journals, Books and some research papers related to the research work will be completed. Further we will place order for the chemicals which will use for the preparation of thin films.

Year II – Plan:

In second year, efforts have been taken for the preparation of good quality NiO, Li doped NiO and Mn doped NiO thin films by chemical method. The structural, morphological, optical and electrical properties of prepared film will be studied by using XRD, SEM, UV-VIS spectrophotometer and two probe/four probe measurement system.

Year III – Plan:

In the last year, we will prepare Research papers to send them for the publication in reputed journals at an national and international level. Further we will submit the final thesis of the proposed work for doctoral degree.

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